[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A Simple Proof of the Thermodynamic Stability of Materials Taken Up by Solutions Containing Solubilizers Such as Soap

BY JAMES W. MCBAIN AND JOHN J. O'CONNOR

It has commonly been assumed that an *emulsion* of a volatile liquid in water would have the same vapor pressure as the volatile liquid in bulk, or one even greater due to the curvature of the droplets. The function of an emulsifying agent has then been limited to provide a coating to prevent coalescence of the droplets.

It is the object of this communication to show that colloidal solutions of otherwise insoluble materials in detergents are thermodynamically stable in that their formation is accompanied by a lowering of free energy. The vapor pressure of an insoluble volatile liquid taken into colloidal solution by a solubilizer is far less than that of the volatile liquid alone. It is only when excess above this is added that there is any emulsion.

Our previous communications have shown that colloidal electrolytes in solution are as stable as true solutions such as sugar or salt. They also have shown that these colloidal electrolytes and many other solubilizers can extend some of their stability to insoluble dyes, extracting them from unsaturated non-aqueous solution and producing true reversible equilibria.

In water the solubility of ether or hydrocarbon or dye is very greatly increased by the presence of soap, and the formation of the colloidal solution is accompanied by a decrease in the activity of the organic material and a decrease in the free energy of the system.

The organic substances here investigated are diethyl ether, petroleum ether, methylcyclopentane and hexane. Both the actual increase in solubility caused by the presence of soap and the effect of the soap upon the vapor pressure of the volatile solute have been observed. In some cases unsaturated vapor has been dissolved by soap solution with further reduction in vapor pressure.

Before examining any of the experimental numbers with the hydrocarbons, emphasis must be laid upon the fact that in comparison with the effects recorded the lowering of vapor pressure, either of water or of hexane, by the soap may be completely neglected. Even the strongest soap solution used could only lower the vapor pressure of water by 0.024 mm., and all others by lesser amounts; whereas effects up to 150 mm. are involved. Likewise the insolubility of the soap in hexane or methylcyclopentane prevents it from lowering the vapor pressure by any such Raoult mechanism. Finally, hexane and water notoriously have mutual zero solubility and therefore do not affect each other's vapor pressure.

I. Experiments Done with Apparatus Shown in Fig. 1

Figure 1 shows a symmetrical all-glass apparatus whose two legs are connected by a mercury manometer, from which the mercury may be withdrawn by lowering the reservoir to permit free intercommunication of the vapors. Liquids are added on both sides through the stopcocks shown. Stirring is provided for by placing in each leg a sealed glass bulb containing iron filings which can be continuously and slowly raised and lowered by solenoids outside, the whole being immersed in a thermostat at 25°. Before use the apparatus is

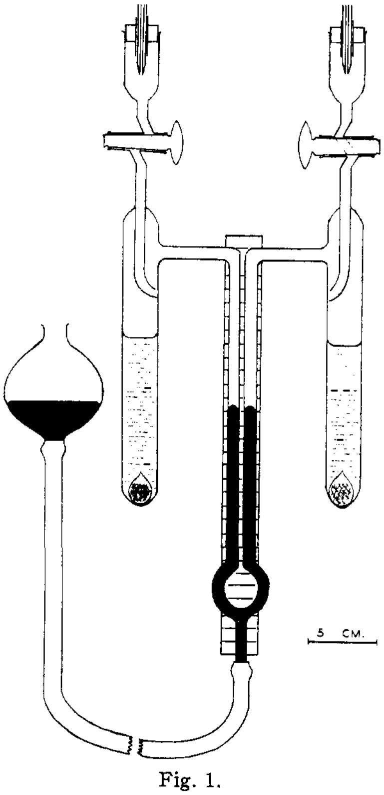

Fig. 1.

evacuated and the solutions then added to the two sides.

A. Addition of Soap Causes Hexane to Dissolve in Water and then Progressively Lowers its Vapor Pressure by as Much as 50%.—When water is added to each leg of the apparatus in Fig. 1, and then to one side is added a visible amount of hexane, the difference in vapor pressure due to free hexane is shown by the manometer. To the water–hexane side a solution of potassium oleate (made from Merck oleic acid of equivalent weight 288.4 and iodine number 93.5, with potassium hydroxide pellets containing 3% carbonate) is added progressively in small amounts. After each addition the solution is stirred until the vapor pressure becomes constant. The soap is seen to cause solution of the hexane. The initial pressure difference due to free hexane is 149 mm., and this is only slightly affected until the hexane visibly disappears. Further addition of soap then causes progressive lowering as shown in Table I which records a typical experiment.

TABLE I

DIFFERENCE IN VAPOR PRESSURE BETWEEN WATER AND A SYSTEM OF WATER–HEXANE WHEN SOAP IS ADDED TO THE LATTER

Soap concn., g./1000 g. H_2O	Vapor press. diff., mm.	Soap concn. g./1000 g. H_2O	Vapor press. diff., mm.
0.000	149	37.7	103
5.80	147	41.3	97.5
11.20	146	44.8	92
16.4	143	48.1	88
21.2	134	51.1	83.5
25.6	126.5	54.0	79
29.9	118	56.9	76.5
33.9	110.5	59.6	74

The effect of the soap is more apparent if these results are contrasted with the effect of adding pure water to water in equilibrium with a partial pressure of hexane less than that of the saturated value. Such results are given in Table II, where water is added to 25 cc. of a water–hexane system in equilibrium with about 50 cc. of vapor space.

TABLE II

EFFECT OF ADDING WATER TO A WATER–HEXANE SYSTEM CONTAINING A PARTIAL PRESSURE OF HEXANE OF 120 MM. AT 25°. SATURATED PARTIAL PRESSURE OF HEXANE AT THIS TEMPERATURE IS 149 MM.

H_2O added, cc.	Vapor press. diff., mm.	H_2O added, cc.	Vapor press. diff., mm.
0	120	5	127
1	121	7	129.5
3	124	9	132.5

The solubility of hexane in water is so slight that the addition of water to a water–hexane system causes an actual increase in vapor pressure due to compression of the unsaturated vapor space above the water.

B. Addition of Soap Progressively Lowers the Partial Pressure of Ether in Water by as Much as 10%.—An aqueous solution containing 5 g. of ethyl ether per 100 g. of water was placed in each half of the thoroughly evacuated apparatus. Thereupon to one side progressive amounts of potassium oleate solution containing the same amount of ether per 100 g. of water were added, and to the other side an equal volume of the original ether–water solution was added. This eliminated any effects due to the decrease in vapor space and the result is the same as if solid potassium oleate were added to one side. After each addition of soap the solution was stirred until the reading of the manometer became constant. The results are shown in Table III, where it is seen that the vapor pressure is lowered by the soap in almost direct proportionality to the amount added. It should be mentioned that the original pressure of the solution was 367 mm. and that as already stated the Raoult lowering of vapor pressure due to added soap is negligible in comparison with the effects observed.

TABLE III

DIFFERENCE IN VAPOR PRESSURE BETWEEN 5 G. OF ETHER IN 100 G. OF WATER AND THE SAME SOLUTION CONTAINING POTASSIUM OLEATE

Soap added, g./1000 g. H_2O	Lowering, mm.	Soap added. g./1000 g. H_2O	Lowering, mm.
0.00	0	19.40	28.3
3.86	5.6	21.90	32.0
7.43	10.8	24.27	35.1
10.76	16.3	26.52	37.6
13.81	21.7	28.63	39.5
16.73	26.9		

C. Sodium Silicate Raises the Partial Pressure of Ether in Water.—Salts have the opposite effect from soap. They salt out and raise the vapor pressure, and sodium silicate does likewise. Analyzed sodium silicate containing a ratio $SiO_2/Na_2O = 3.19$, was obtained from the Philadelphia Quartz Company. On one side of the apparatus was placed progressive amounts of ether solution containing 5 g. of ether per 100 g. of water, and on the other side equal volumes of first the same solution and then additional solution containing added silicate. It is seen in Table IV that now the vapor pressure is raised by silicate, again in almost direct proportion to the silicate added.

TABLE IV

DIFFERENCE IN VAPOR PRESSURE BETWEEN 5 G. OF ETHER IN 100 G. OF WATER AND THE SAME SOLUTION CONTAINING SODIUM SILICATE

Silicate added, g./1000 g. H_2O	Increase, mm.	Silicate added, g./1000 g. H_2O	Increase, mm.
0.00	0.0	17.97	25.6
3.52	4.7	20.18	28.5
6.81	9.9	22.60	31.1
9.53	14.5	24.70	34.1
12.73	18.4	26.70	35.8
15.42	21.9		

D. Addition of Sodium Silicate Raises the Vapor Pressure of Ether in Soap Solution, but in Equal Weight the Net Effect of Both is a Lowering.—Since soap and silicate exert opposite effects, equal weights of the silicate and the oleate were added in the 5 g. of ether per 100 g. of water, as shown in Table V, where the net effect is a small lowering of vapor pressure.

TABLE V

DIFFERENCE IN VAPOR PRESSURE BETWEEN 5 G. OF ETHER IN 100 G. WATER AND THE SAME SOLUTION CONTAINING EQUAL WEIGHTS OF POTASSIUM OLEATE AND SODIUM SILICATE

Soap per 1000 g. H_2O, g.	Lowering, mm.	Soap per 1000 g. H_2O, g.	Lowering, mm.
0	0	17.24	6.9
3.46	.3	20.1	9.0
6.70	.8	22.4	10.8
9.75	1.6	24.4	12.4
12.56	3.4	26.4	13.8
15.21	5.0		

II. Experiments Done with Apparatus in Fig. 2, with Volatile Hydrocarbons Insoluble in Water

Figure 2 shows an apparatus in which a volatile hydrocarbon is contained in a narrow graduated tube which permits direct reading of the amount that vaporizes and dissolves in the soap solution in the other leg. The two are connected through a stopcock which may be closed from time to time to read on the mercury manometer the vapor pressure above the aqueous solution. Thus the driving force or thermodynamic free energy of the process is determined at each stage. Direct isothermal distillation is observed up to the point where the aqueous liquid becomes saturated with hydrocarbon. Arrangement is again made for stirring the aqueous solution in the thermostat.

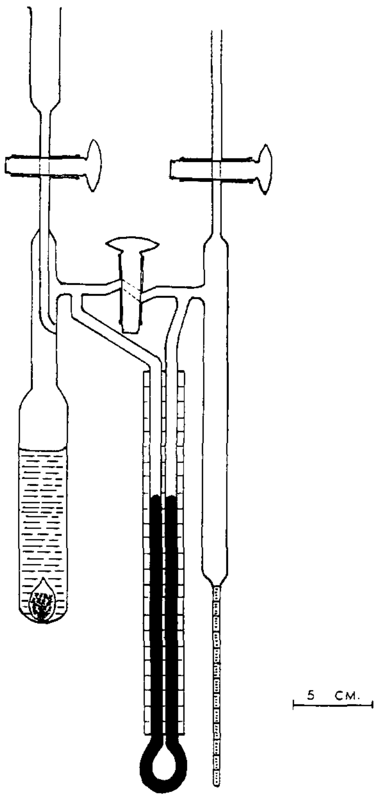

Fig. 2.

E. Liquid Methylcyclopentane and Petroleum Ether, as Well as Hexane, Distil into a Soap Solution of the Same Temperature.—Preliminary experiments were done before including the manometer. It was observed that about 6 g. of petroleum ether per liter of soap solution disappeared into 5.62 g./100 cc. oleate solution without the process coming to an end. Similar observations were made with hexane and methylcyclopentane which are superseded by the more systematic measurements under the next heading.

F. The Vapor Pressure of Methylcyclopentane or of Hexane Rises Progressively from Zero to its Normal Value when about 1.8 to 2.0% Has Dissolved in Soap Solution.—To begin an experiment the hydrocarbon is placed in the graduated capillary tube which is then chilled with liquid air while the whole apparatus is thoroughly evacuated. The communicating stopcock is closed and the soap solution added. In order to remove small amounts of air invariably dissolved therein, the soap solution is alternately stirred and evacuated until the vapor pressure difference between the two sides of the apparatus becomes constant. Less than 0.1 cc. of water is thus removed, which is a negligible proportion.

A small amount of water is now added to the side containing the hydrocarbon and it is so manipulated as to cause it to condense as a mist on the upper walls of the apparatus. This precaution ensures saturation of the entire apparatus with water. Otherwise the results are distorted in the following manner: the first rapid diffusion prevents water vapor from reaching the hydrocarbon side until the rate is sufficiently slow for back diffusion to be effective. Thus the apparent vapor pressure of the hydrocarbon is too great until the later stages of distillation, and this may even lead to the appearance of a minimum in the curve of apparent vapor pressure plotted against amount. distilled. The points in Figs. 3 and 4 represent the constant values finally arrived at in each stage

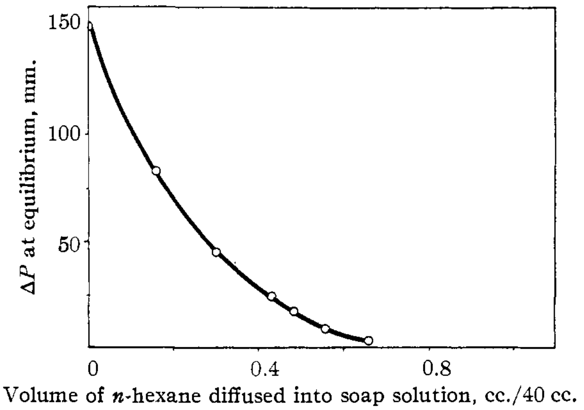

Fig. 3.—The difference in vapor pressure between hexane–water and soap solution dissolving progressive amounts of hexane.

Figure 3 gives the data for the spontaneous distillation of *n*-hexane into 5.62 g./100 cc. potassium oleate of *p*H 10.56. It is seen that saturation is not attained until about 0.7 cc. of *n*-hexane has diffused through the vapor phase to dissolve in 40 cc. of soap solution.

Figure 4 gives on its main curve similar data for the spontaneous solution of methylcyclopentane in the same potassium oleate solution. It is seen that over 0.8 cc. of methylcyclopentane is dissolved per 40 cc. of soap solution.

G. Silicate and Alkali both Enhance the Solubility and the Lowering of Vapor Pressure of the Volatile Hydrocarbons in Soap Solutions.—Figure 4 includes the curves of results showing that if the 5.62 g./100 cc. potassium oleate solution contains also 0.2% of SiO_2 added as sodium silicate of ratio SiO_2/Na_2O = 3.19 and of *p*H still 10.56, or instead 0.121 *N* potassium hydroxide, the solubility of the hydrocarbon is enhanced. With the added potassium hydroxide it is evident that the soap solution would dissolve about 20% more hydrocarbon. The added silicate and the *p*H are those which Woo[1] found the optimal with water-insoluble dye.

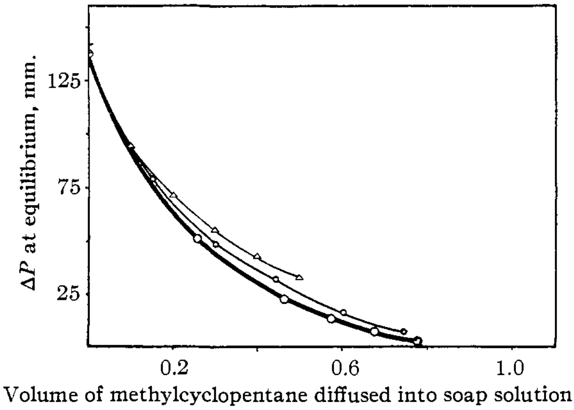

Fig. 4.—The difference in vapor pressure between methylcyclopentane + water and methylcyclopentane dissolving in progressively larger amounts in potassium oleate solution as such, or with addition of sodium silicate or of excess potassium hydroxide.

Discussion

Previous communications[1,2] from this Laboratory demonstrated that aqueous solutions of detergents dissolve dyes which are normally insoluble in water, forming solutions that are thermodynamically stable in that they enter into true reversible equilibria and their properties are solely dependent upon temperature, composition and pressure. The present observations afford a particularly clear basis for such conclusions. They show that until a certain definite amount has been taken up, an amount that is enormously greater than that which can dissolve in pure water, the detergent solution is still unsaturated, and the vapor pressure lies well below that of the free hydrocarbon.

This solubility in detergent solutions, or dilute solutions of solubilizers such as bile salts, is clearly not mere emulsification, which would have produced, if anything, the opposite effect upon the combined vapor pressures of the two mutually saturated liquids. Neither is it mere protective action which likewise would have left the vapor pressure unaltered or more probably enhanced due to curvature. It cannot possibly be true solution

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[1] J. W. McBain and Ts-Ming Woo, *Kolloid-Z.*, **87**, 74 (1939).

[2] J. W. McBain and M. E. L. McBain, THIS JOURNAL, **58**, 2613 (1936); McBain and Woo, *ibid.*, **60**, 223 (1938); *J. Phys. Chem.*, **42**, 1099 (1938); *Kolloid-Z.*, **87**, 74 (1939).

of single independent molecules of hydrocarbon in the dilute aqueous medium, because this is still essentially water and large amounts of other ordinary solvents are required to modify it. Hence, it must involve some kind of association with the dissolved detergent itself. It may well involve the different kinds as well as sizes of colloidal micelles which various authorities agree to preëxist in the soap solutions themselves. Kiessig and Philippoff in Hess's laboratory[3] have proven by X-ray measurements of clear solutions of benzene in soap solution that some, at least, of the benzene is sandwiched between the lamellar micelles whose spacing is correspondingly increased in the direction normal to the lamellar faces to which the soap molecules themselves are normal.

Colloidal particles are visible in the ultramicroscope in all cases so far tested where a sufficiently dilute detergent solution has taken up nearly the saturation amount of water-insoluble material. There are no microscopically visible particles or droplets. The unsaturated solutions of hydrocarbon appear clear until they near saturation. Hartley's suggestion that it is mere solution in the water-insoluble portion of the detergent micelle is in disagreement with his own data with Miss Parsons showing that the amount taken up was fivefold greater. It is likewise out of accord with the fact, shown in Fig. 4, that the addition of a small amount of silicate increases the solubility of a hydrocarbon in the soap solution, where by itself it has no solvent action whatsoever.

It has been known since 1874 that *concentrated* soap solutions dissolve cresols and tar oil, and the important paper of Engler and Dieckhoff,[4] in which a clear distinction is made between solution and emulsification, has been generally overlooked or forgotten. They made numerous measurements of the dissolving power of soap solutions for hydrocarbons, fatty acid, phenols and mixtures. These effects are of great importance in pharmacy, cosmetics and industry. The action of solubilizers is of vital importance in biological processes.

Summary

Hydrocarbons, such as methylcyclopentane, normally insoluble in water dissolve to the extent, in this case, of 0.19 mole/liter in 0.18 mole/liter potassium oleate solution, and to an even greater extent in soap solutions containing small additions of silicate or hydroxide. The colloidal solutions formed are thermodynamically stable because the vapor pressure is significantly less than that of the free hydrocarbon until the solution is approximately saturated.

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[3] H. Kiessig and W. Philippoff, *Naturwiss.*, **27**, 593 (1939).

[4] C. Engler and E. Dieckhoff, *Arch. Pharm.*, **230**, 561 (1892).

[CONTRIBUTION FROM THE PHYSICAL-BIOLOGICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Hydrogen Bridging in Cellulose as Shown by Infrared Absorption Spectra

BY JOSEPH W. ELLIS AND JEAN BATH

As early as 1926 it was predicted by Sponsler and Dore[1] that the orientation of the cellulose chains in the cell walls of naturally occurring Ramie fibers is stabilized laterally by secondary valence forces associated with the hydroxyl groups of the glucose residues. Similar suggestions have been made by Huggins in a review of hydrogen bridging in organic compounds[2] and by Mark in a recent review of the X-ray investigations on carbohydrates.[3] It is the purpose of this paper to cite evidence for these suggestions on the basis of infrared absorption studies.

By means of a correlation of X-ray investigations with the model proposed by the organic chemists it was initially shown by Sponsler and Dore[1] and later by Meyer and Mark[4] that cellulose may be thought of as consisting of long, chain-like molecules, which in the case of Ramie fibers lie approximately parallel to the fiber axis. The fundamental repetition unit of 10.3 Å. along the axis of the long molecule was shown to correspond to the calculated length of one anhydrocellobiose unit consisting of two *β-d*-glucose residues united by a glucosidic linkage between carbons 1 and 4 of the two pyranose rings as seen

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[1] O. L. Sponsler and W. H. Dore, *Colloid Symposium Monograph*, **IV**, 174 (1926).

[2] M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1938).

[3] H. Mark, *Chem. Rev.*, **26**, 169 (1940).

[4] K. H. Meyer and H. Mark, *Ber.*, **61**, 593 (1928); *Z. physik. Chem.*, **B2**, 115 (1929).